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ON THE FORMATION OF PEROXIDE COMPOUNDS IN THE LOW-BOILING FRACTIONS OF ESTONIAN SHALE TAR

[Ob obrazovanii perekisnykh soedinenii v nizkokipyashchikh fraktsiyakh estonskoi slantsevoi]

Anne Casberg

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On the Formation of Peroxide Compounds in the Low-Boiling Fractions of Estonian Shale Tar

Anne Castern

The formation of resin is a phenomenon long known to petrochemical science. Although its chemical nature is not entirely clear, it is thought that the process is determined by highly saturated hydrocarbons such as diene and triene and is the result of autooxidation accompanied by polymerization and polycondensation; the result is a resinous product which diminishes the antiknock properties of petroleum gasolines [1]. In the case of shale tar, resin formation was investigated essentially in terms of the use of such tar as engine fuel. It is thought that resin formation in shale tar is determined not only by the oxidation of olefins, but also by neutral oxygen compounds, which appear to be the primary resin-forming agents [2, 3]. Besides diolefins, sulfur compounds also contribute to resin formation in gasolines [1]. Our data, which are based on the distillation of a neutral oil separated from the phenolate of shale gasoline, confirm this fact. The content of sulfur compounds in the oil amounted to 3.6%. Fractions with boiling points 130--145° C and 160--170° C, in which sulfur content was 6--8% due to the accretion of thiophene derivatives, changed into a heavy, viscous mass after a short storage time.

Since our study on the composition of neutral oxygen compounds of shale tar with boiling points of 200° or less [5] involved continual contact with the phenomenon of resin formation, some data are provided below on the origin and composition of the autooxidation products of this shale tar fraction.

After 2--3 months storage at room temperature, fractions of tunnel resin (boiling points 66--145°) precipitate a light-brown, oxygen-rich, viscous phase to the bottom of the vessel. Mixtures with high oxygen

content were also obtained by the adsorption-chromatograph separation of fractions with b. p. $\leq 180^{\circ}$ in a column with aluminum oxide upon washing with acetone or methanol. Positive results were achieved by the reaction of a peroxy group with an acid solution of potassium iodide [6]. Resin formation was not observed in fractions with b. p. $> 180^{\circ}$ due to the presence of phenols, which are powerful oxidation inhibitors.

We made a more detailed study of peroxide compounds extracted from a tunnel resin fraction with b. p. 157--183°. The fraction was separated chromatographically in a column with aluminum oxide. The ratio of adsorbent to separated substance was 10:1; petroleum ether, benzene, and acetone served as elutriating agents. The results of the chromatographic separation are given in the Table.

Results of the Adsorption-Chromatograph Separation of a Fraction of Tunnel Resin (157--183°) and Properties of the Fractions Obtained.

Fraction	Fraction weight, g	n_D^{20}	d_{20}^{20}	Oxygen content,%
I	7.0	1.4455	0.755	--
II	2.5	--	--	--
III	1.8	--	--	--
IV	0.3	1.4835	0.875	--
V	0.25	1.4460	0.851	8.9
VI	0.95	1.4550	0.865	16.7
VII	2.1	1.4270	0.908	31.0

The oxygen content of the fractions was determined by the method described in reference [7]. In fraction VII the content is approximately twice that of fraction VI which (as shown by gas chromatographic analysis) contains carbonyl compounds. The fact that fraction VII exhibits a reaction which is also characteristic of peroxy groups

suggests that it may contain peroxide compounds formed as a result of storage or during chromatographic separation.

Fig. 1 shows the gas chromatograms of fractions VI and VII. The fact that fraction VII, which is more strongly adsorbed on aluminum oxide, emerges more quickly from the polar polyglycol column contradicts the general principles of chromatographic separation.

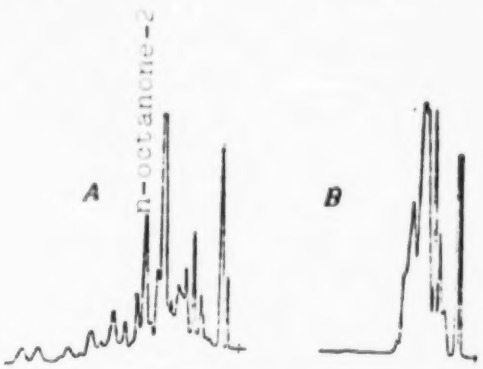

Fig. 1: Gas chromatograms; A - of carbonyl (fraction VI) and B - of peroxide compounds (fraction VII) separated from a tunnel resin fraction with b. p. 157--183° C.

Chromatographic conditions: 6-m column with 15% polyethylene glycol of celite 545, temp. 170°, hydrogen consumption approx. 60 ml/min.

In view of the thermal instability of peroxy compounds, however, the contradiction disappears if we notice that the chromatogram obtained is characteristic not of the original peroxide compounds, but of their decomposition products. It is well known that peroxide compounds have poor thermal stability and for this reason often cannot be analyzed by gas-chromatographic methods [8]. Data is available on the gas-chromatograph separation of some peroxides in a helium stream [9], but it must be considered that this experiment was performed under rather mild conditions: moderate temperature, short columns, and storage of the peroxides in solution.

The thermal decomposition of peroxides is strongly dependent on the conditions of the reaction. The presence of seemingly insignificant amounts of impurities or temperature fluctuations may affect relative product yields or even the decomposition mechanism. At 100--250° in the liquid or gas phase, depending on the structure of the original compound, the decomposition products consist of various alcohols, ethers, aldehydes, ketones, formaldehyde, acetone, CO_2, CO, H_2, and O_2 [6].

Fig. 2 shows the gas chromatograms of the products of the decomposition of the investigated peroxide compounds on an active platinum catalyst (5% Pt/silica gel ShSK) at 350°, and on a low-activity platinum catalyst (5% Pt/chromosorb W) at 300°. In the first case, low-molecular hydrocarbons are formed (C_1--C_3), even in a large amount of water; in the second case, the primary decomposition product is acetone.

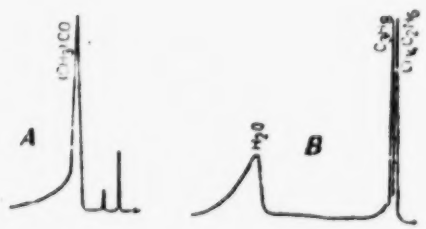

Fig. 2: Gas chromatograms of the decomposition products of compounds of fraction VII; A - catalyst 5% Pt/chromosorb W, temperature 300° C; B - catalyst 5% Pt/silica gel type ShSK, temp. 330°.

The formation of peroxide compounds was also observed upon storage of the olefin fraction of tunnel resin with b. p. 66--110°. The decomposition products of these compounds included formaldehyde, which was also detected among the decomposition products of peroxide compounds of the other fractions studied. It was determined that the autooxidation

of olefins is accompanied by the formation of polymeric peroxides, the decomposition products of which are usually those carbonyl compounds formed by the ozonization of corresponding monomeric olefins [8]. Since 1-olefins are a predominant constituent of shale tar [10], the presence of formaldehyde among the decomposition products was not unexpected.

The determination of the exact composition of peroxides is a laborious task, which calls for a variety of analytical techniques in addition to chromatography. Suitable standard substances -- pure peroxides -- are also needed.

Conclusions

Based on a study of the composition of a shale tar fraction with b. p. $\leq 180^{\circ}$, it was determined that when this fraction is stored at room temperature for several months, peroxide compounds of an olefin origin are formed.

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